LEBANESE AMERICAN UNIVERSITY

School of Arts and Sciences-Beirut
Division of Natural Sciences
Chemistry Department

Organic Chemistry (I) Laboratory
CHM313Lab

Properties and Reactions of Alcohols (R-OH) and Phenols (Ar-OH)

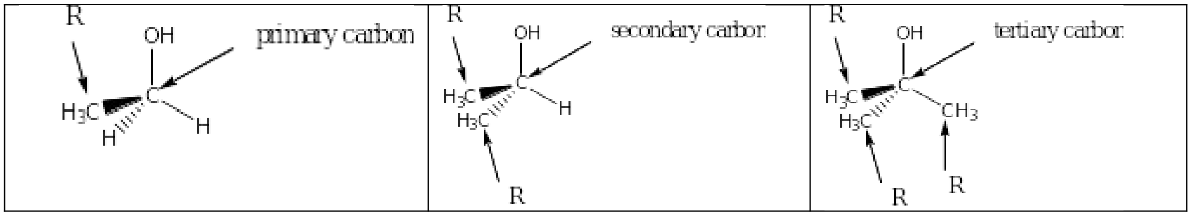
Background Information

Introduction

The general formula of an alcohol is ROH in which the R is an aliphatic hydrocarbon group. Alcohols may be looked upon as derivatives of water, HOH. One hydrogen of water is substituted by an alkyl group, R. Like water, alcohols show hydrogen bonding. As the chain of the R group increases the hydrocarbon character of the compound overshadows the polar character of the OH group. Consequently, the solubility and boiling point of an alcohol are affected by the length of the carbon chain and the shape of the molecule. The short chain alcohols are soluble in water, whereas the longer chain alcohols are insoluble in water. In general a molecule which is more compact (i.e., more branched) will be more soluble in water and will have a lower boiling point than the straight chain isomer. Phenols are aromatic alcohols, in which R is an aromatic ring. This experiment will demonstrate some of the properties of alcohols and phenols.

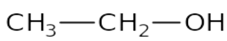
Although alkyl alcohols have an -OH group, they do not ionize in water, whereas phenols ionize like acids (donating a proton to water). The -OH group of alkyl alcohols can be positioned on different carbon atoms of the carbon chain and are classified as primary (1°), secondary (2°), or tertiary (3°) alcohols depending on whether the -OH group is attached to a carbon with 1, 2 or 3 other carbon atoms attached to it.

Primary alcohol:	***Secondary alcohol:***	***Tertiary alcohol:***

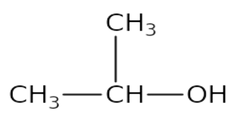


The International Union of Pure and Applied Chemistry (IUPAC) method of nomenclature for alcohols use the ending **<u>ol</u>**. Change the 'e' ending of an alkan***<u>e</u>*** to ***<u>ol</u>*** (*i.e.* methan**<u>e</u>** to **<u>ol</u>** → methan**<u>ol</u>;** ethan**<u>e</u>** to **<u>ol</u>** → ethan**<u>ol</u>**).

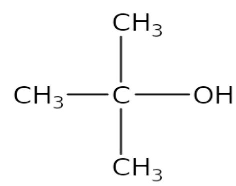
These different alcohols react differently with Lucas reagent and with Bordwell-Wellman reagent; hence these reagents can be used for identifying the class of alcohol. The relative acidity of phenols can be used to characterize this class of alcohols relative to the alkyl alcohols. This property will be exploited in the identification of phenol.



ethanol
(primary)

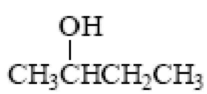


2-propanol
(secondary)

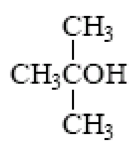


2-methyl-2-propanol
(tertiary)

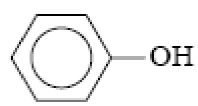
1-Butanol



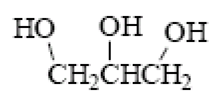
2-Butanol
(sec-butyl alcohol)



1,1-Dimethyl ethanol
(tert-butyl alcohol)



Phenol

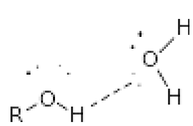


Glycerol
(glycerin)

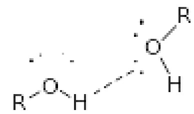
<u>Physical Properties of Alcohols:</u>

1- Alcohols are colorless at room temperature.

2- Alcohols form hydrogen bonds with water.



3- Alcohols form intermolecular hydrogen bonds (with itself). This causes alcohols to have higher boiling points than hydrocarbon of similar molecular mass.



4- **Solubility of Alcohols in Water:**
Alcohols with 5 or less carbon atoms are soluble in water. The hydroxyl group present in all alcohols is a polar functional group. The polarity of this group allows alcohols to form hydrogen bonds. Small chain alcohols are able to mix with water because of the hydrogen bonding interactions that will occur between the hydroxyl functional group and the water. ***If the R-group of the alcohol becomes too large however, the solubility of the alcohol will decrease.***

Solubility of Phenols in Water:** ***Phenol is moderately soluble in water - about 8 g of phenol will dissolve in 100 g of water. If you try to dissolve more than this, you get two layers of *liquid*. The top layer is a solution of phenol in water, and the bottom one a solution of water in phenol. The solubility behavior of phenol and water is complicated. Phenol is somewhat soluble in water because of its ability to form hydrogen bonds with the water.

Chemical Properties of Alcohols:

1- Reaction with Sodium:
If a small piece of sodium is dropped into some ethanol, it reacts steadily to give off bubbles of hydrogen gas and leaves a colorless solution of sodium ethoxide, CH_3CH_2ONa. Sodium ethoxide is known as an *alkoxide*. If the solution is evaporated carefully to dryness, the sodium ethoxide is left as a white solid.

$$\mathbf{R\text{-}OH + 2Na \rightarrow 2R\text{-}ONa + H_2 \uparrow (g)}$$

Alkoxide   Hydrogen gas

$$2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2ONa + H_2$$

Although at first sight you might think this was something new and complicated, in fact it is exactly the same (apart from being a more gentle reaction) as the reaction between sodium and water. Compare the two:

$$2CH_3CH_2\text{-}OH + 2Na \longrightarrow 2CH_3CH_2\text{-}ONa + H_2$$

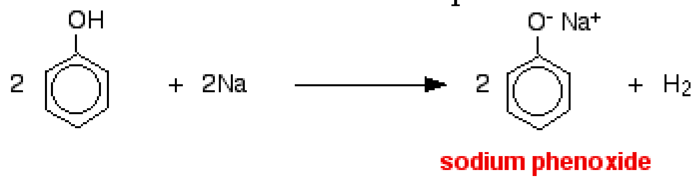
$$2H\text{-}OH + 2Na \longrightarrow 2H\text{-}ONa + H_2$$

We normally, write the sodium hydroxide formed as NaOH rather than HONa - but that's the only difference. Sodium ethoxide is just like sodium hydroxide, except that the hydrogen has been replaced by an

ethyl group. Sodium hydroxide contains OH^- ions; sodium ethoxide contains $CH_3CH_2O^-$ ions.

Phenols with Sodium: ***Acids react with the more reactive metals to give hydrogen gas. Phenol is no exception - the only difference is the slow reaction because phenol is such a weak acid.***

Phenol is warmed in a dry tube until it is molten, and a small piece of sodium added. There is some fizzing as hydrogen gas is given off. The mixture left in the tube will contain sodium phenoxide.



2- Lucas Test:

This test is for low molecular weight alcohols and it distinguishes the rates of reaction of alcohols with the Lucas reagent (HCl and $ZnCl_2$). Positive indicator of the reaction is the formation of a water insoluble alkyl chloride as cloudiness or a precipitate. The formation of an alkyl chloride with tertiary alcohol is very rapid, followed by the secondary alcohol that may take from 5 to 20 minutes to form visible cloudiness. Primary alcohols do not react with Lucas reagent or it may show very little result in a very long time.

3º alcohol: $R_3COH + HCl\ (ZnCl_2) \rightarrow R_3Cl$ (alkyl chloride) + H_2O **[Very Fast]**

(Insoluble/cloudiness)

2º alcohol: $R_2CHOH + HCl\ (ZnCl_2) \rightarrow R_2CHCl$ (alkyl chloride) + H_2O **[Slow]**

(Insoluble/cloudiness)

1º alcohol: $RCH_2OH + HCl\ (ZnCl_2) \rightarrow$ ***No reaction*** **[Very Slow]**

(No cloudiness)

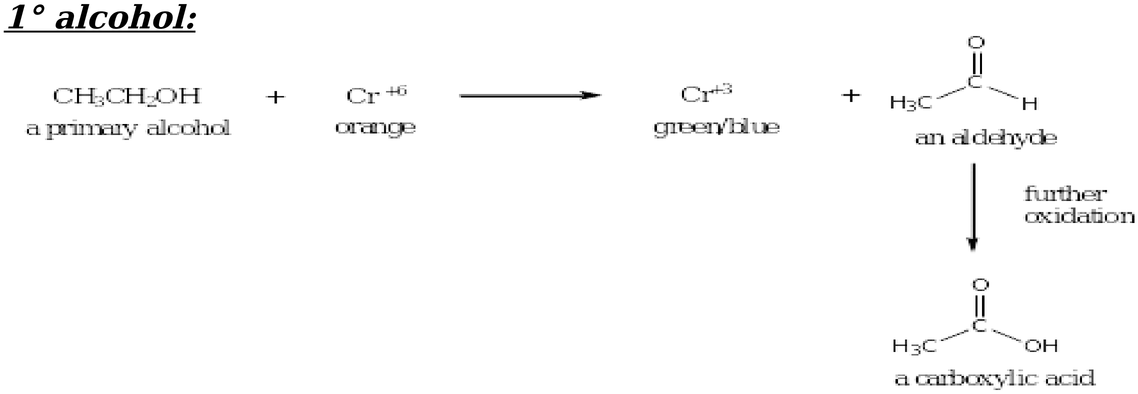
Phenols*:* $ArOH + HCl\ (ZnCl_2) \rightarrow$ ***No reaction***

3- The Bordwell-Wellman Test [Chromic acid]

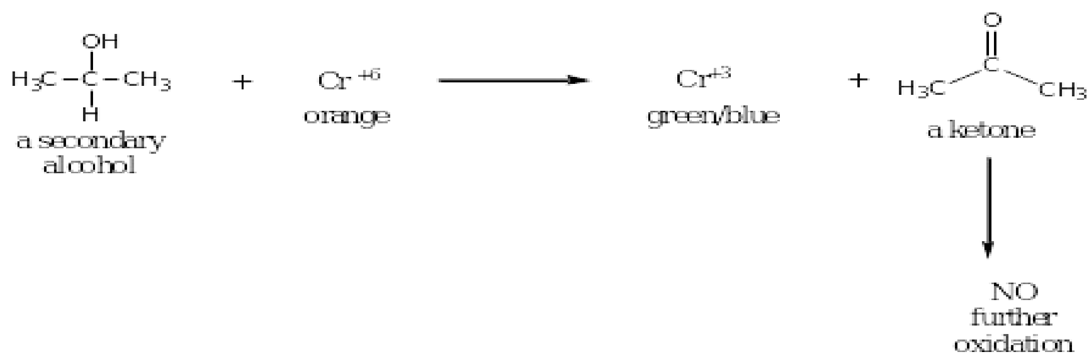
Oxidation of alcohols by strong oxidants such as $K_2Cr_2O_7$ in H_2SO_4 is possible, but differs depending on the degree of alcohol. The examples below show how a primary, secondary, and tertiary alcohol respectively responds to treatment of oxidants. If a reaction has

occurred using $K_2Cr_2O_7$ in H_2SO_4, there is a color change from orange to green.

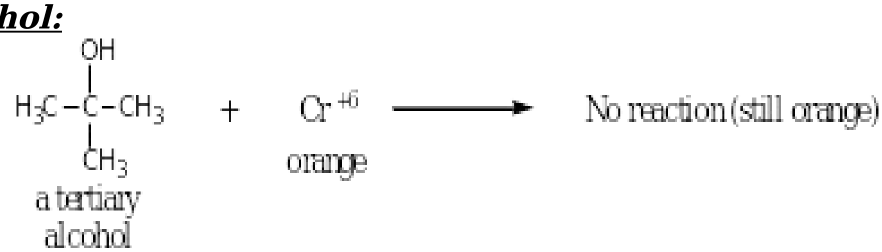
1° alcohol:



2° alcohol:

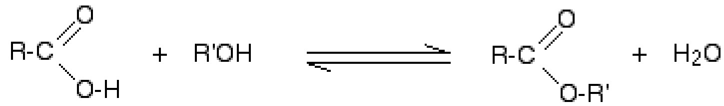


3° alcohol:

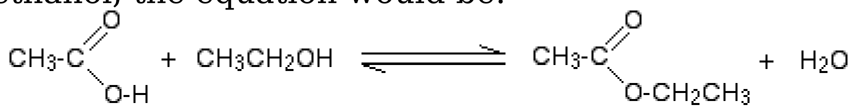


4- Esters Formation:

Esters are produced when carboxylic acids are heated with alcohols in the presence of an acid catalyst. The catalyst is usually concentrated sulfuric acid. Dry hydrogen chloride gas is used in some cases, but these tend to involve aromatic esters (ones containing a benzene ring). The Esterification reaction is both slow and reversible. The equation for the reaction between an acid RCOOH and an alcohol R'OH (where R and R' can be the same or different) is:

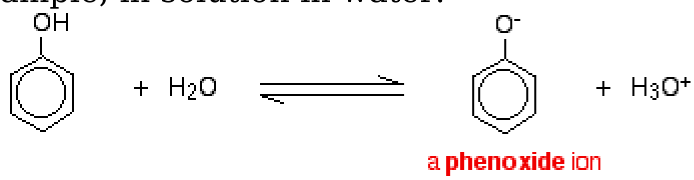


So, for example, if you were making ethyl ethanoate from ethanoic acid and ethanol, the equation would be:



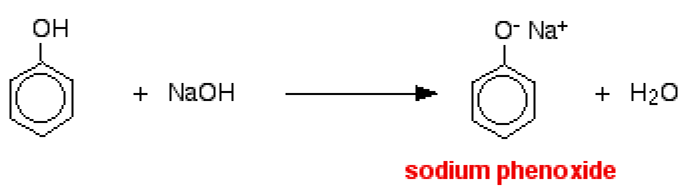
5- Acidity of Phenols:

Unlike alcohols (which also contain an -OH group) phenol is a weak acid. A hydrogen ion can break away from the -OH group and transfer to a base. For example, in solution in water:



Phenol is a very weak acid and the position of equilibrium lies well to the left.
Phenol can lose a hydrogen ion because the phenoxide ion formed is stabilized to some extent. The negative charge on the oxygen atom is delocalized around the ring. The more stable the ion is, the more likely it is to form. One of the lone pairs on the oxygen atom overlaps with the delocalized electrons on the benzene ring. This overlap leads to a delocalization which extends from the ring out over the oxygen atom. As a result, the negative charge is no longer entirely localized on the oxygen, but is spread out around the whole ion. Spreading the charge around makes the ion more stable than it would be if all the charge remained on the oxygen. However, oxygen is the most electronegative element in the ion and the delocalized electrons will be drawn towards it. That means that there will still be a lot of charge around the oxygen which will tend to attract the hydrogen ion back again. That's why phenol is only a very weak acid.

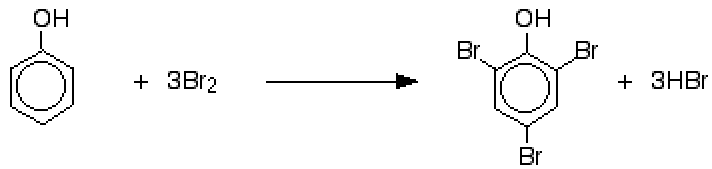
Phenol reacts with sodium hydroxide (NaOH) solution to give a colorless solution containing sodium phenoxide.



In this reaction, the hydrogen ion has been removed by the strongly basic hydroxide ion in the sodium hydroxide solution.

6- Reaction of Phenols with Bromine water:

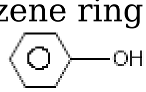
If bromine water is added to a solution of phenol in water, the bromine water is decolorized and a white precipitate is formed which smells of antiseptic.
The precipitate is 2,4,6-tribromophenol.



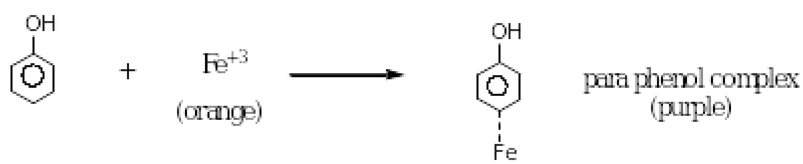
2,4,6-tribromophenol

Notice the multiple substitutions around the ring - into all the activated positions.

7- Reaction of Phenols with Ferric Chloride:

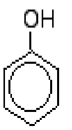
Phenolic compounds have a benzene ring with the –OH group attached to the benzene ring carbon atom. The simplest compound is phenol (C_6H_5OH) or .

Phenols are considered very weak acids. They have different physical and chemical properties from alcohols. They neither undergo oxidation nor react with the Lucas reagent. However, phenols react with $FeCl_3$ [Ferric Chloride or Iron(III) chloride] to form a *para*-phenol-Fe complex (which has an intense violet-purple color).



Iron(III) ions form strongly colored complexes with several organic compounds including phenol. The color of the complexes varies from compound to compound. The reaction with iron(III) chloride solution can be used as a test for phenol.

Properties and Reactions of Alcohols (R-OH) and Phenols (Ar-OH)

	Primary alcohol:	***Secondary alcohol:***	***Tertiary alcohol:***	***Phenol:***
				
# of Carbons				
Solubility in Water				
Solubility in NaOH				
Lucas Test- HCl and $ZnCl_2$				
The Bordwell-Wellman Test [Chromic acid]- $K_2Cr_2O_7$ in H_2SO_4				
Bromine water				

Ferric Chloride				